



Influence of electrical gradients in the migration of ions in red earth

Sivapullaiah PV¹, Shankara², Maya Naik³, Rama Krishna⁴

1. Professor, Department of Civil Engineering, Indian Institute of Science, Bangalore-560012, India. E-mail ID: siva@civil.iisc.ernet.in, telephone: +91-80-2293 2672(O), fax: +91-80-23600404
2. Assistant Professor, Dept. of Civil Engineering, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Bangalore 560035, India, E-mail ID: bcreative_shank@yahoo.com
3. Professor, Dept. of Civil Engineering, BMS College of Engineering, Bull Temple Road, Bangalore-560 019, India, Email: snmcivbmsce@gmail.com
4. Department of Environmental Studies, Institute of Science, GITAM University, Visakhapatnam 530045, India, Email: chrk2020@gmail.com

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General Note

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ABSTRACT

Efforts are made to bring out the influence of application of electrical gradient on the migrations of sodium cation and chloride anion through compacted kaolinitic red earth soil. For this purpose sodium chloride solution is passed through the soil compacted in an electro kinetic cell by applying hydraulic gradient and electrical gradient in the same direction; and they are in the opposite direction. Breakthrough curves of these ions have been obtained for both sodium and chloride ions under these conditions. It has been shown that the diffusion coefficient of sodium is higher when the electrical gradient and with hydraulic gradient are in the same direction than when they are in the opposite directions. The reverse is same for chloride ion. Thus for effective removal of sodium both hydraulic gradient and electrical gradient should be in the same direction and for chloride the electrical gradient should be in the opposite direction of hydraulic gradient.

Keywords: Chloride ion, Diffusion coefficient, Electrokinetic, Osmotic flow, Sodium ion

1. INTRODUCTION

Past practices have resulted in a number of contaminated sites in proportion to the industrial output. The large production of wastes in modern society often poses a threat to ground water quality and already have resulted in many incidents of ground water contamination. The leachates generated in waste fills migrate down wards and poses threat to ground water contamination unless properly contained by barriers. Natural clay deposits or re-compacted clayey liners act as barriers. Fine grained soils retard the migration of ions. Under these circumstances the movement of contaminants will be slow and controlled primarily by diffusion. The clay itself can also act as an important medium for attenuation of some contaminants due to processes such as sorption, precipitation and biodegradation (Maya Naik and Sivapullaiah, 2003, Sivapullaiah and Nagendra prakash, 2007). Application of electokinetic principle for effective removal of ions is advocated for the removal of ions.

1.1. Electrokinetic Process for Remediation of Contaminated Sites

In general water can flow through porous media not only in response to a gradient in total hydraulic head and chemical composition (chemico-osmosis) but also in response, to gradient in electricity (Electro-osmosis), and temperature (thermal osmosis). In the absence advective flow, solute can migrate through porous material not only response to a concentration gradient but also in response to an electrical gradient (Electro phoresis) and thermal gradient (thermal diffusion). These additional flow processes typically are referred to as coupled flow processes in order to distinguish them from direct flow processes represented by advection and diffusion (Fang, 1997, Sivapullaiah and Nagendra prakash, 2007) Use of electrical potential is made to decontaminate fine grained soils.

1.2. Migration of Ions under Electrical Gradient

Fine-grained soils are difficult to clean with microbiological treatment or soil washing processes, because of the high adsorption capacity and the low bio-availability (Alshawabkeh and Yueng, 1999) Also, because of low hydraulic conductivity the pump treat technology is impractical. The large specific area of the fine-grained soil provides numerous active sites for surface complexation and sorption of contaminants. These reactions reduce the quantity of contaminants in the dissolved phase and thus reduce the cleanup efficiency of most remediation technologies. If these reactions are permanent and irreversible, they can be used to solidify and stabilize the contaminants in situ. Unfortunately, many of these reactions are dynamic, pH dependent, and reversible. Therefore, the attenuation of contaminant transport provided by these reactions cannot be considered as a permanent contaminant containment mechanism. Electro remediation involves passage through soil of direct current between appropriately distributed electrodes, which is effective for fine grained soils of low hydraulic permeability (Page and C.L., 2002, Sivapullaiah and Nagendra prakash, 2007) Mechanisms by which water and solutes are transported through soils under applied electrical fields may involve several contributory processes whose relative importance varies from one system to another. These are

1. Electro-osmosis: movement of soil moisture or groundwater from the anode to the cathode.
2. Electro migration: movement of ion or ion complexes within the soil moisture or groundwater.

Electro-osmotic fluid volume flow rate is described by an equation analogous to Darcy's law

$$Q = k_e I_e A \quad \text{Eq. (1)}$$

Where Q = increased fluid volume rate on application of electrical potential (m^3/s);

k_e = coefficient of electro-osmotic conductivity ($\text{m}^2/\text{V-s}$);

I_e = electric field strength (V/m);

A = total cross sectional area perpendicular to the direction of fluid flow.

Electro-osmotic flow rate depends on the balance between the electrical force on the liquid and the friction between the liquid and the surface of the soil particles (Albert et al., 1995).

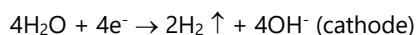
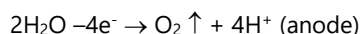
Values of hydraulic conductivity for different types of soils can vary many orders of magnitude. However, values of coefficient of electro-osmotic conductivity of different soils lie in the narrow range of 1×10^{-9} to 1×10^{-8} $\text{m}^2/\text{V}\cdot\text{s}$. Therefore, an electric field is a much more effective in driving fluid through fine-grained soils of low hydraulic conductivity than a hydraulic gradient and vice versa for coarse-grained soils of high hydraulic conductivity. During an electrokinetic extraction process, the applied DC electric field can thus drive an effective electro-osmotic advection of contaminant through the soil and/or inject enhancement agents into the contaminated soil.

The electro-osmosis transport mechanism is necessary for contaminants to move towards electrode. The more saturated the soil, the easier electrolysis will occur.

From existing literature, the average electro-osmotic mobility has been calculated to be in the order of 5×10^{-9} m^2/Vs , where U is potential drop and is equal to V/m.

Electrolysis and Electro-migration

An electric field causes the following reactions at the electrodes (electrolysis of water):



The pH value will drop at the anode and it will increased at the cathode. According to the electrolysis reactions the produced ions move corresponding to their charge to the electrode of opposite polarity. This causes a pH gradient in the soil.

In the case of Electro-osmosis and electrophoresis, one considers only water transport or particle transport respectively; with electrolysis only the movement of ions and ion complexes are taken into consideration.

The applied DC electric field can induce ionic migration of contaminants. Ionic migration or electro migration is the movement of charged chemical species relative to the movement of pore fluid. Anions (negatively charged ions) are moved towards the anode (positive electrode) and cations (positively charged ions) are moved towards the cathode (negative electrode). Cationic contaminants migrate towards region where they are precipitated. If the pH value in the soil is not regulated, heavy metals will precipitate. This means that heavy metals will only be concentrated in the soil but not removed (Do-hyung et al., 2009, Gray and Mitchell, 1967). The removal of cations by ion migration is enhanced by electro-osmosis as both mechanisms cause the cations to migrate towards the cathode. However, the ionic migration mechanism of the anions toward the anode may be diminished by electro-osmosis. Ionic migration is the dominant migration mechanism. Therefore, anionic contaminants can be removed at the anode though electro-osmosis moves the anions in the opposite directions (Yeung and Mitchell, 1993)

Combining the mechanisms of electro-osmotic advection and ionic migration results in the applicability of electro-kinetic extraction. Electrophoresis is avoided by applying a low voltage which cannot induce clay particle migration. The current required is usually on an order of mAcm^{-2} of cross-sectional area between the electrodes (Yeung and Mitchell, 1993, Sivapullaiah, 1997).

The efficiency of removal of cations near cathode is advantageous when the electrical gradient is in the same direction of hydraulic gradient. The net removal efficiency of cations depends on the amount of osmotic flow generated and ion migration however the removal efficiencies vary considerably with type of cation and the nature of soil. In this work the removal efficiency of conservative sodium ion from kaolinitic soil is studied. The removal of anions at anode can also be considered but may not be very effective as osmotic flow and ion migration are in the opposite directions (Alshawabkeh and Yueng, 1999). Electro osmotic flow is not beneficial as it is in the direction of anode to cathode and anions have to remove at the anode. The removal essentially depends mainly on ion migration only. Further the hydraulic head will decrease due to opposing osmotic flow. Migration is effective when the anion is not strongly adsorbed on the clay in the soil. Thus the removal of anions depends on the relative effects of osmotic flow and ion migration. Chloride is also conservative ion and is not adsorbed on the clay more particularly on kaolinite mineral (Do-hyung et al., 2009). Thus, in this paper, the removal efficiencies of sodium and chloride ions are studied when the hydraulic gradient and osmotic flow are in the same direction and when they are in the opposite direction for both sodium ion and chloride ion.

2. MATERIALS AND METHODS

2.1. Soil Used

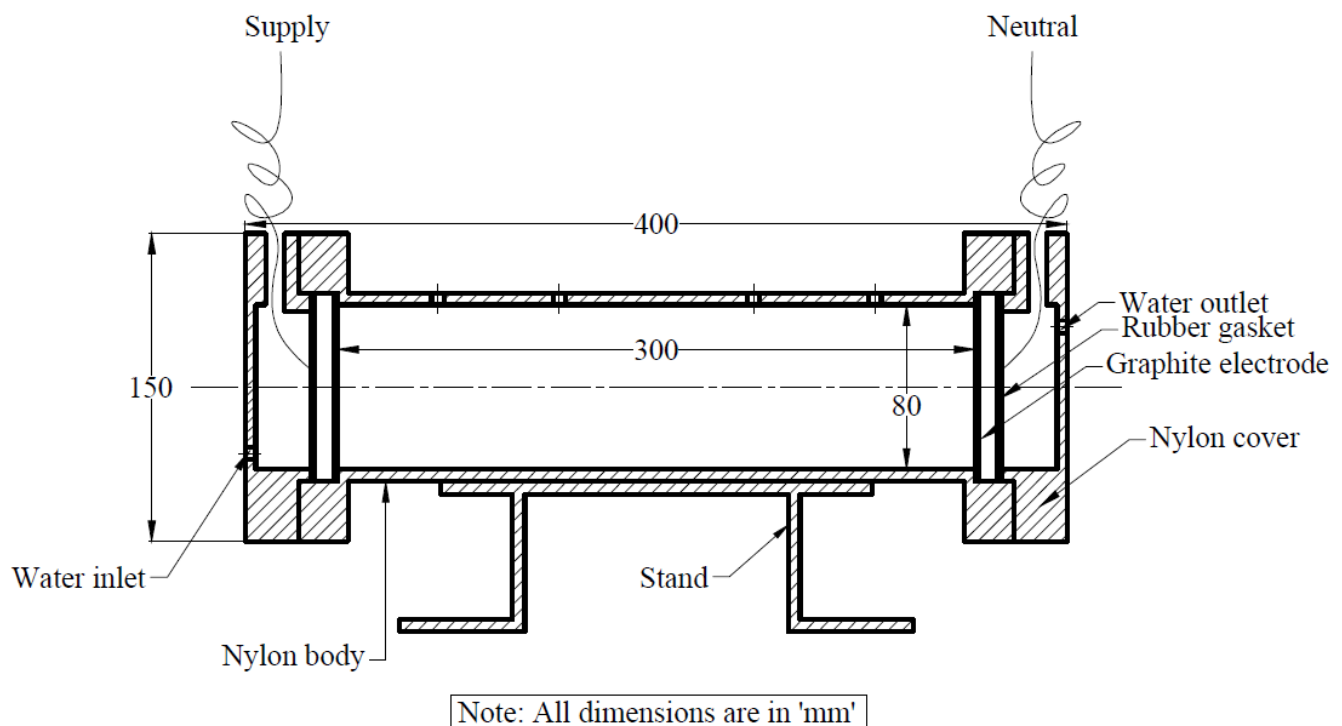
Red Earth used in this study was obtained from Indian Institute of Science campus Bangalore, India. The soil was collected by open excavation from a depth of one meter from the natural ground. The soil was dried and passed through IS sieve size of 425 microns. The soil so obtained has clay content of 35%. The clay content consisted predominantly of kaolinitic mineral. The cation exchange capacity of the soil was about 12.2 meq/100gms. The physico Chemical and index properties of soil are given in table 1.

Table 1 Properties of Soils used

Property	Red Earth
Specific Gravity	2.73
Liquid Limit (%)	34.9
Plastic Limit (%)	17.7
Shrinkage Limit (%)	13.6
Clay Content (%)	35
Max Dry Density (kN/m ³)	17.9
Optimum Moisture Content (%)	16.2
Cation Exchange Capacity, (meq/100g)	12

2.2. Apparatus for Electro-Kinetic Studies

A new electro kinetic apparatus was designed, fabricated for this study. The hydraulic pressure of inlet is controlled independently by "Self Compensating Mercury Control "device. The Electro-kinetic cell was fabricated using nylon material, which is a non-conductor of electricity, corrosive resistant, not affected by acid or alkali. The electrokinetic cell consists of two end caps and a specimen cylinder made up of nylon. The test sample was 80 mm in diameter and 300 mm long. The end caps house the graphite plate electrodes, inflow and outflow tubings. Normal grade graphite perforated plates were used. Holes of 1mm dia were drilled through the graphite plate electrode to facilitate water transport during electro-osmosis. Details of electrokinetic cell are shown in Fig. 1. The required electrical circuit has been designed, connected and assembled. Provision has been made to pass water through the soil compacted in the cell. The hydraulic pressure head of inlet fluid is 100 kPa.

**Figure 1** Electro-kinetic Extraction Cell

2.3. Sample Preparation

The oven dried soil was mixed with water thoroughly to ensure homogeneous distribution of contaminants and kept in a polythene bag and placed in a humid desiccator overnight to achieve uniform moisture content. The soil is then compacted in the cylinder to bring it to 85% of maximum dry density on dry of optimum 2% on the compaction curve. The soil is divided into three equal parts by weight and then each part is emplaced into the specimen cylinder and compacted one by one using a screw jack to ensure uniform compaction for the entire specimen.

After compaction, the perforated electrodes were covered with the filter papers and the end caps were closed. Fluid in-let and out let tubes was connected to the cell. Then water was passed through the cell under a specific constant hydraulic head using the self-compensating mercury control device and saturated.

Then the sodium chloride solution containing 1000 ppm of sodium and 1544 ppm of chloride is passed through the Electrokinetic cell under a gradient of 1 meter from anode to cathode for experiments with hydraulic flow and osmotic flow in the same direction and from cathode to anode when osmotic flow is in the opposite directions. The rate of flow of the leachate through the soil cell is monitored. It was found that the average rate of flow was in the range of $8.94 \times 10^{-3} \text{ cm}^3/\text{sec}$. The concentrations of sodium and chloride in the out flow are determined and breakthrough curves are plotted.

3. RESULTS AND DISCUSSION

Breakthrough curves represent the temporal variations in the concentration of a solute at the effluent end of a column of a porous material. Breakthrough curves can be measured using laboratory columns by:

1. Establishing steady-state fluid flow condition.
2. Continuously introducing at the influent end of the column a liquid containing a solute at a concentration C_0 ; and
3. Monitoring the solute concentration at the effluent end.

The breakthrough curves which are normally obtained for solute migrating under advection and diffusion, in this case, represent for ions migrating under combined influence of advection, diffusion and electrokinetic force. The breakthrough curves of sodium and chloride ions are obtained when the electrical flow and hydraulic flows are in the same direction and in the opposite direction.

3.1. Migration of Sodium Ions under Combined Influence of Electrical and Hydraulic Potential when they are in the Same Direction

3.1.1. Variation of Relative Concentration of Sodium Ions with Number of Pore Volumes

Figure 2 shows the variation of relative concentration of sodium with number of pore volumes of sodium chloride solution passed through the cell. From the graph, it can be observed that the arrival of $C/C_0 = 0.5$ concentration is at 3.25 pore volumes of flow and for the arrival of $C/C_0 = 1$ more than 4.5 pore volumes of flow has occurred. It was shown in Chapter 2 that ions, which are not retarded, will C/C_0 of 0.5 at 1 Pore Volume. But due to random dispersion tends to spread the front so that some chemicals arrive before 1 Pore Volume. In this case even with application of electrical gradient in the direction of hydraulic flow and tends to accelerate the migration of positive sodium ions towards cathode faster, the breakthrough is only at 4 pore volumes. This shows that sodium is strongly retarded by red earth. Sodium is not usually retarded by soils since it can replace the exchangeable divalent ion and whatever small retardation present may only be due to surface adsorption. The reasonable strong retardation of sodium is due to removal of calcium present in the exchangeable complex of the clay to form less soluble calcium chloride and consequent occupation of sodium in the exchangeable sites. These ions so adsorbed are not significantly desorbed by application of electrical potential of 1 V/cm. (Maya Naik and Sivapullaiah, 2003, Sivapullaiah, 1997) earlier observed it that sodium breakthrough occurs at about 4.5 pore volumes under application of advection without electrical gradient. Application of voltage has reduced the number of pore volumes required for breakthrough from 4.5 to 4.0. However, the time required for breakthrough is reduced considerably due to increased flow due electro-osmosis.

However, the applicability of these methods for ions migrating under combined influence of hydraulic, chemical and electrical gradient is not established. In this study, these approached have been used and their relative advantages will be studied.

3.1.2. Variation of Relative Concentration of Chloride Ions with Number of Pore Volumes

Figure 3 shows the variation of relative concentration of chloride with number of pore volumes of sodium chloride solution passed through the cell. From the graph, it can be observed that the arrival of $C/C_0 = 0.5$ concentration is at 2.9 pore volumes of flow and for the arrival of $C/C_0 = 1$ more than 3.36 pore volumes of flow has occurred.

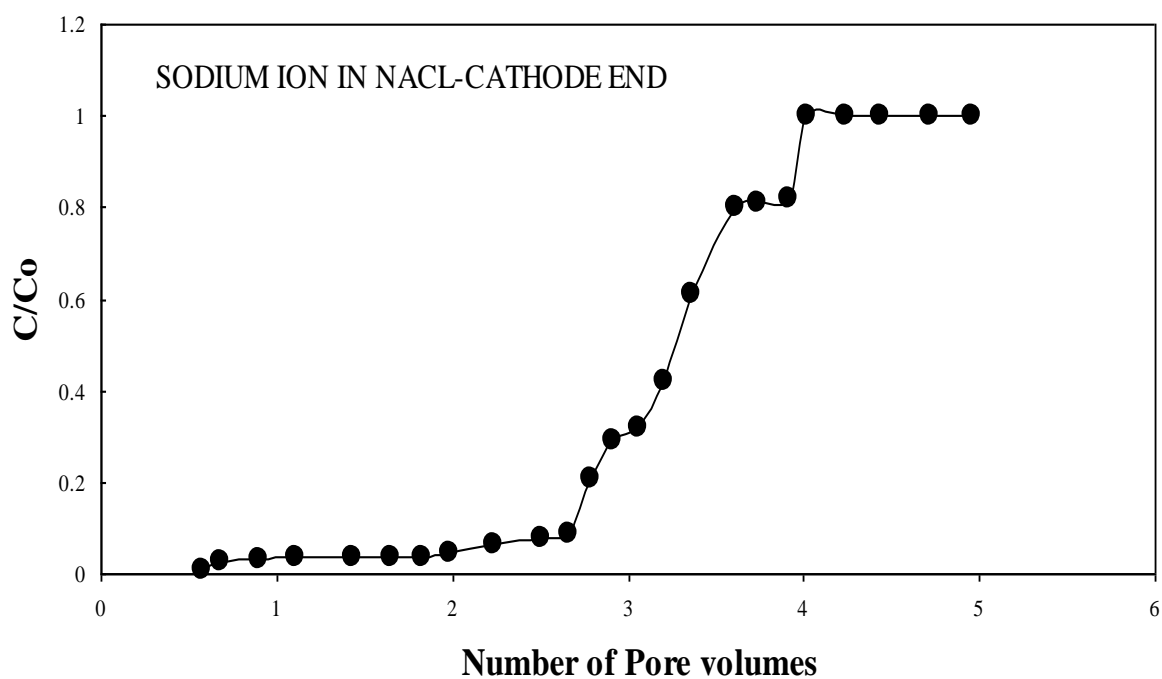


Figure 2 Variation of relative concentration of sodium with number of pore volumes of sodium chloride solution passed through the cell

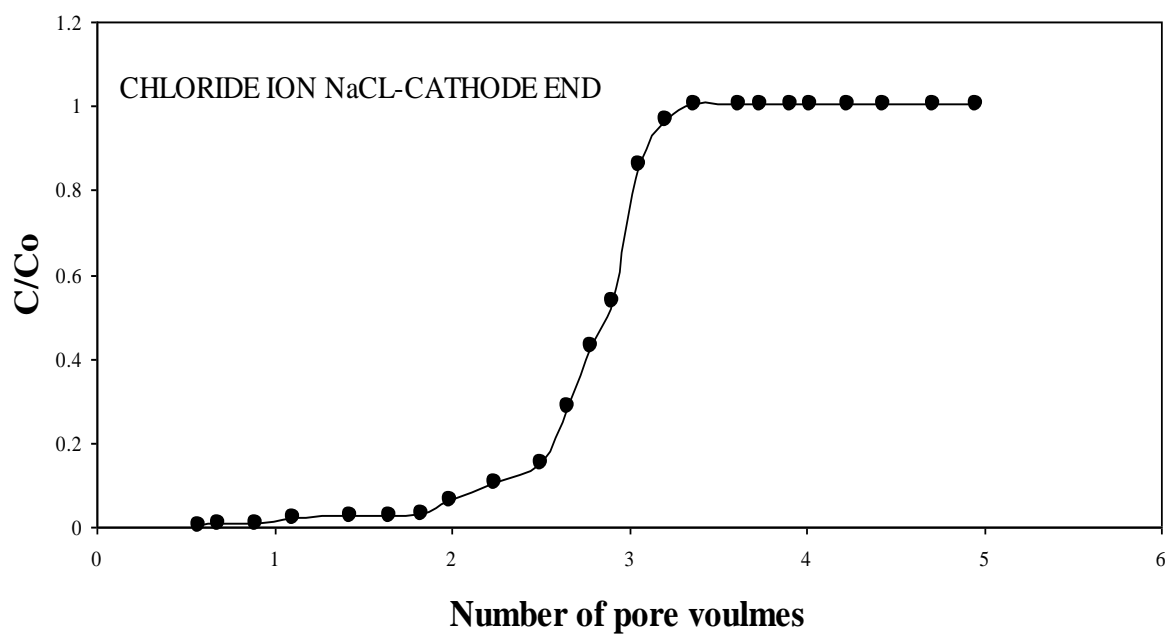


Figure 3 Variation of relative concentration of chloride with number of pore volumes

3.2. Migration of ions under combined influence of electrical and hydraulic potential when they are in the opposite direction

3.2.1. Variation of Relative Concentration of Sodium Ions with Number of Pore Volumes

Figure 5 shows the variation of relative concentration of sodium with number of pore volumes of sodium chloride solution passed through the cell. From the graph, it can be observed that the arrival of $C/C_o = 0.5$ concentration is at 6.90 pore volumes of flow and for the arrival of $C/C_o = 1$ more than 9.43 pore volumes of flow has occurred.

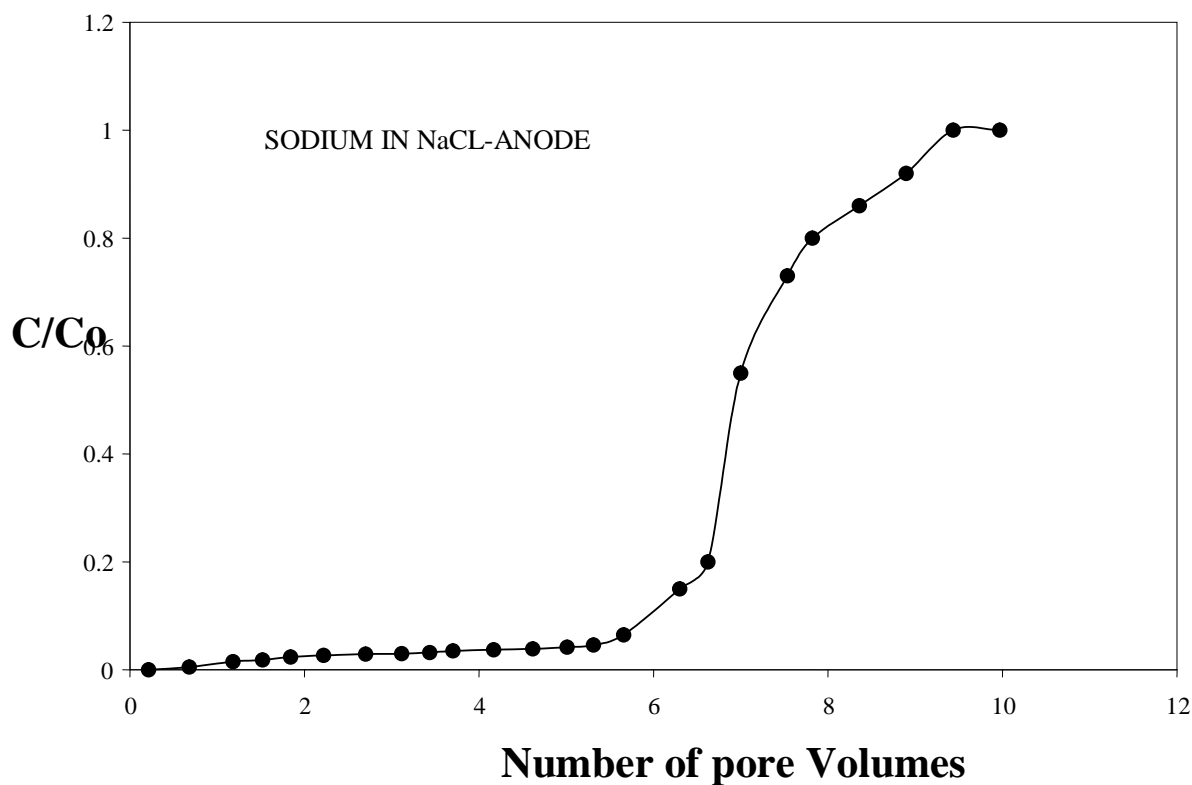


Figure 4 Variation of relative concentration of sodium with number of pore volumes of solution in opposite direction

Figure 4 shows the variation of relative concentration of chloride with number of pore volumes of sodium chloride solution passed through the cell. From the graph, it can be observed that the arrival of $C/C_o = 0.5$ concentration is at 2.9 pore volumes of flow and for the arrival of $C/C_o = 1$ more than 3.36 pore volumes of flow has occurred.

3.2.2. Variation of Relative Concentration of Chloride Ions with Number of Pore Volumes

Figure 5 shows the variation of relative concentration of chloride with number of pore volumes of sodium chloride solution passed through the cell. From the graph, it can be observed that the arrival of $C/C_o = 0.5$ concentration is at 1.7 pore volumes of flow and for the arrival of $C/C_o = 1$ more than 2.5 pore volumes of flow has occurred.

3.3. Determination of Effective Diffusion Coefficients

In general, methods used to calculate the transport parameters fall into two broad categories-steady and transient states. Several transient methods have been used to calculate transport parameters. This soil column test, traditionally known as leaching column test has been used to study adsorption and migration of contaminants. First steady state flow is established through the soil sample by using distilled water in the source reservoir. After steady state fluid has been established, the fluid in the influent reservoir is

changed to a solution with known and constant concentration (C_0) of particular chemical constituents. The concentration (c) in the effluent reservoir is measured as a function of number of pore volumes. Then C/C_0 , versus pore volumes of flow (Sivapullaiah, 1997). Though there different methods to calculate effective diffusion coefficients, Root Time method has been used in this paper.

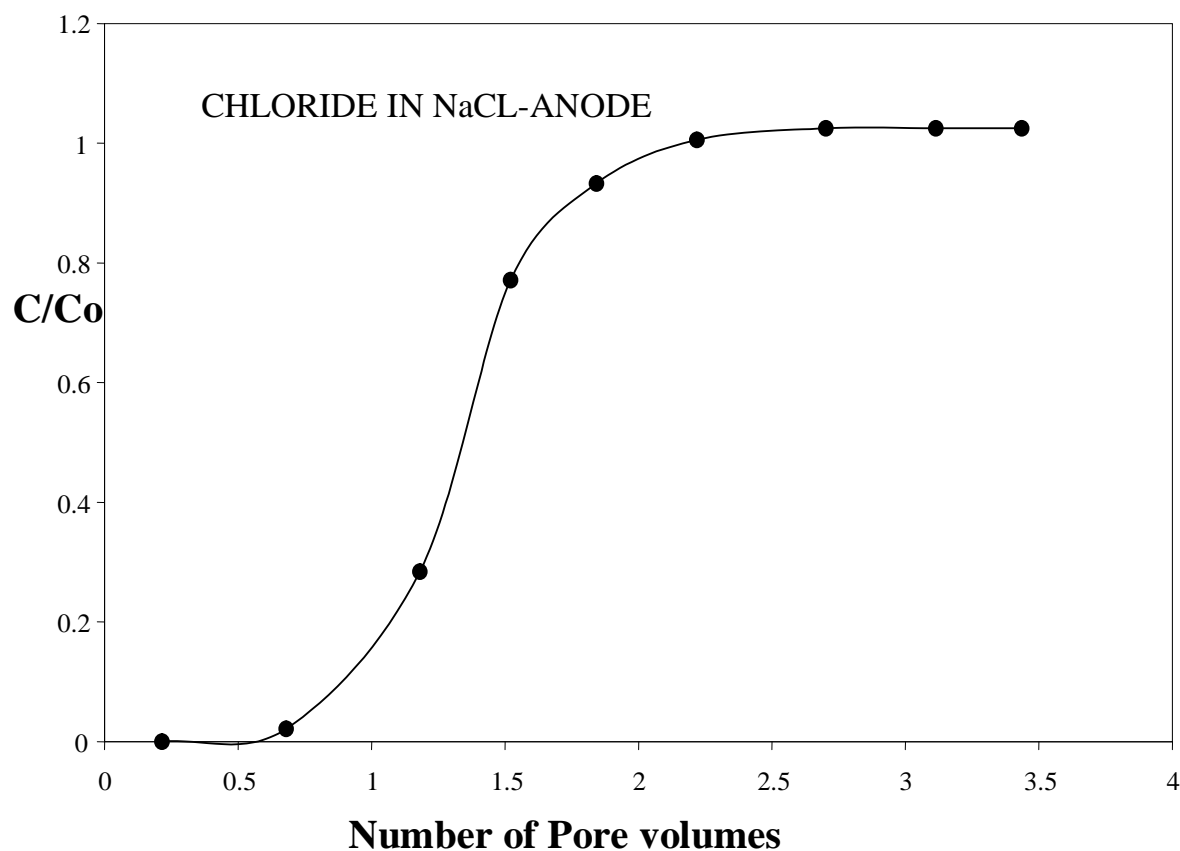


Figure 5 Variation of relative concentration of chloride with number of pore volumes of sodium chloride solution opposite direction

Root Time Method

In this method, the time corresponding to relative concentration of 0.1 (90% equilibrium) is obtained from the breakthrough curve of the species. Then diffusion coefficient, D , is calculated using the equation,

$$D = \frac{0.2436L^2}{t_{90}}$$

Table 2 Calculation of effective Diffusion coefficient of ions under different conditions using Root Time method

Sl.No.	Particulars	For Na ion When osmotic flow and hydraulic flow are in the same direction	For Na ion When osmotic flow and hydraulic flow are in the opposite direction	For Cl ion When osmotic flow and hydraulic flow are in the same direction	For Cl ion When osmotic flow and hydraulic flow are in the opposite direction
1	Length of the column (cm)	30	30	30	30
2	Velocity (cm/sec)	2.572E-04	3.165E-03	2.572E-04	3.165E-03
3	t_{90} in hours	128	90	120	18
4	$D_e = 0.2436L^2/T_{90}$ cm ² /sec	4.758 E-04	6.767-04	5.075 E-04	3.383 E-03

4. CONCLUSIONS

1. The number of breakthrough pore volume at which the breakthrough occurs is less for sodium ion when the electrical flow and hydraulic flow are in the same direction. The reverse is true when the electrical flow and hydraulic flow are in the opposite direction.
2. The number of breakthrough pore volumes at which the breakthrough occurs is more for chloride when the electrical flow and hydraulic flow are in the opposite direction.
3. The number of breakthrough pore volumes for sodium ion is more compared the electrical flow and hydraulic flow in the same direction and in the opposite direction.
4. The number of breakthrough pore volumes for chloride ion is more with electrical flow and hydraulic flow in the same direction and in the opposite direction than with compared with the column experiment.
5. The effective diffusion coefficient of sodium is lower when the hydraulic gradient and electrical gradient are in the same direction than when they are in the opposite directions.
6. The effective diffusion coefficient of sodium is higher when the hydraulic gradient and electrical gradient are in the same direction than when they are in the opposite directions.

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